PREPARATION OF STEREOISOMERIC 1,4-DISUBSTITUTED BUT-2-EN-1,4-DIOLS AND PROOF OF THEIR CONFIGURATION

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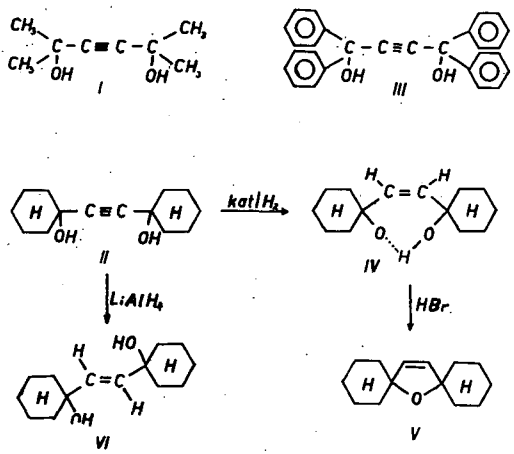
Experiments were carried out concerning the hydrogenation of 1,4-disubstituted but-2-in-1,4-diols and it was found that in the case of catalytically activated hydrogenation the rate and capability of hydrogenation, moreover the stereospecificity of the process is in connection with the space-requirement of the 1,4-substituents.

Comparative results were obtained with 10% Pd-charcoal catalyst: compound I was hydrogenated fast to yield a mixture, II took up hydrogen slowly to yield the cis.-olefin diol. Compound III could be hydrogenated very slowly and in case of less active catalyst no hydrogenation at all took place.

With $LiAlH_4$ 1,1,4,4-tetramethylbut-2-in-1,4-diol (I) gave 1, 1,4, 4,-tetramethylbutan-1,4-diol, while 1,2-bis-(1-hydroxycyclohexyl)-acetylene afforded stereospecifically cis-1,2-bis-(1-hyroxy-cyclohexyl)-ethylene.



The steric structure of the geometrical isomer cis- and trans-1,2-bis-(1-hydroxycyclohexyl)-ethylene prepared in the course of our experiments was proved by means of their infrared spectra and application of BRUNI's rule.

The development of our earlier works [1a, b] necessitated the preparation of stereoisometric 1,4-disubstituted but-2-en-1,4-diols. Therefore we examined the hydrogenation of 1,1,4,4-tetramethylbut-2-in-1,4-diol (I) [2], 1,2-bis-(1-hydroxy-cycloexyl)-acetylene (II) [3], and 1,1,4,4-tetraphenylbut-2-in-1,4-diol (III) [4]. In the course of catalytic hydrogenation of similar compounds besides the two-stage saturation of the acetylenic bond multidirectional hydrogenolysis was observed

and studied in details [5]. In accordance with our purpose reduction experiments with catalitically activated hydrogen and $LiAlH_4$ were carried out.

The saturation reactions with catalitically activated hydrogen were carried out in the presence of Pd precipitated on barium sulphate [6], 10% Pd on charcoal [7], Adam catalyst [8], and Raney Ni.

No hydrogenation occurred with Pd catalyst precipitated upon $BaSO_4$ [6]. On the other hand, the experiments with Pd catalyst on charcoal carrier [7] were successful. In this case the hydrogenation was performed in the presence of 0,3% triethylamine, according to TEDESCHI [5] to minimize undesired hydrogenolysis. Instead of the expected cis-1,1,4, 4-tetramethylbut-2-en-1,4-diol the reaction yielded a mixture of cis- and trans-1,1,4, 4-tetramethylbut-2-en-1,4-diols. On the contrary, 1,2-bis-(1-hydroxycyclohexyl)-but-2-in-1,4-diol (II) afforded cis-1,2-bis-(1-hydroxycyclohexyl)-ethylene (IV) [9], the cis-structure of which was proved by its transformation to 2,5-di-spiro-dicyclohexylyden-2,5-dihydrofuran (V). A further piece of evidence concerning this result is added now by us: the infrared spectrum of the substance, taken in KBr, showed peaks at 1679 and 3200 cm^{-1}, characteristic of cis-olefin derivatives and indicating an intramolecular hydrogen bond, respectively, both supporting the cis structure of (IV).

The Bruni-rule [10], too, was applied and it was found that the compound (IV) is incapable of forming solid solution with 1,2-bis-(1-hydroxycyclohexyl)-ethane.

Under similar conditions the hydrogenation of 1,1,4, 4-tetraphenylbut-2-in-1,4-diol with Pd-charcoal catalyst proceeded only extremely slowly and the substrate was fully saturated to paraffin diol.

Attempts to obtain comparative experimental results with Adams Pt catalyst and Raney Ni failed, but our experiences indicate a decrease in the capability of hydrogenation in the order I' II and III, or rather the hydrogenation fails in case of III and a mixture is resulted from I.

Further on the preparation of 1,4-disubstituted trans-but-2-en-1,4-diols was attempted by reduction with $LiAlH_4$. Such reductions have already been studied [11] and generally the formation of the corresponding trans-isomers was observed [12]. The reduction of bis-1,2-(1-hydroxycyclohexyl)-acetylene with $LiAlH_4$ was carried out to yield a new compound (VI), m. 103—3·5°, having identical molecular formula with cis-bis-1,2-(1-hydroxycyclohexyl)-ethylene (IV), m. 153°. The steric structure of (VI) was proved by means of the Bruni-rule and infrared spectroscopy. It formed solid solution with the corresponding paraffin diol of similar structure and its infrared spectrum showed peaks at 1634 and 3380 cm^{-1}, characteristic of trans-olefin compounds and intermolecular hydrogen bonds, respectively.

The $LiAlH_4$ reduction of 1, 1,4, 4-tetramethylbut-2-in-1,4-diol was also accomplished, however, surprisingly the paraffin diol 1,1,4, 4-tetramethyl-butan-1,4-diol was yielded. In lack of comparative substance the reduction of 1, 1,4, 4-tetraphenylbut-2-in-1,4-diol with $LiAlH_4$ was not examined.

Experimental

Hydrogenation of 1,2-*bis-(*1-*hydroxycyclohexyl)-acetylene* (II) *in the presence of Pd-charcoal.*

0,02 mole 1,2-bis-(1-hydroxycyclohexyl)-acetylene (II) was hydrogenated in 60 ml. methanol-ethanol (1:1) with 0,03 g. 10% Pd-charcoal till the uptake of one

equivalent of hydrogen. The catalyst was filtered off, the filtrate was concentrated *in vacuo* and the residue crystallized from petrol ether, to yield cis-1,2-bis-(1-hydroxy-cyclohexyl)-ethylene [9], m.p. 152—153° C.

Hydrogenation of 1,1,4,4-*tetramethylbut*-2-*in*-1,4-*diol* (I) *in the presence of Pd-charcoal.*

Hydrogenation of 1,1,4,4-tetramethylbut-2-in-1,4-diol (I) under identical conditions as above yielded a product, which on basis of its infrared spectrum was a mixture. Namely, the bands characteristic of acetylene bonding were missing, but the peak characteristic of trans-olefin bond occurred together with a maximum at 1695 cm^{-1}, indicating a cis-olefin structure. The peak at 3290 cm^{-1} further indicated the inhomogeneous character of the substance.

Reduction of 1,1,4,4-*tetramethylbut*-2-*in*-1,4-*diol* (I) *and* 1,2-*bis*-(1-*hydroxycyclohexyl*)-*acetylene* (II) *with* $LiAlH_4$.

200 ml abs. ether and 3,8 g. $LiAlH_4$ were placed in a three-necked flask provided with a dropping funnel, a mechanical stirrer and a reflux condenser and the suspension was vigorously stirred for 5—6 hours. Then a solution of 0.1 mole 1,4.di-substituted but-2-in-1,4-diol (I, II) was added dropwise in 150 ml. ether, the mixture was stirred again for 4—5 hours and kept overnight. Excess $LiAlH_4$ was destroyed with 150 ml. 2N HCl, the ethereal phase was separated, dried, concentrated *in vacuo*, and the residue crystallized from carbon tetrachloride.

The reaction product of 1,1,4,4-*tetramethylbut*-2-*in*-1,4-*diol:*

1, 1,4, 4-tetramethylbutan-1,4-diol [13], m. 93—93.5°C. Anal.: Calc.: $C_8H_{18}O_2$ C 65,76 H 12,32; Found C 65,45 H 11,9. Bromine number O. According to infrared spectrum the substance contains neither acetylenic, nor olefinic double bond.

The reaction product of 1,2-*bis*-(1-*hydroxycyclohexyl*)-*acetylene:*

trans-1,2-bis-(1-hydroxycyclohexyl)-ethylene, m. 103—3.5° C (the cis-compound melts at 153° C). Anal.: Calc.: $C_{14}H_{24}O_2$ C 75,62 H 10,78; Found C 75,31 H 10,35.

Its infrared spectrum shows peaks at 1634 and 3380 cm^{-1}, characteristic of trans-olefin compounds and intermolecular hydrogen bond, respectively.

Formation of solid solution

(Application of Bruni's rule [10a, b]).

a, 1 g. cis-1,2-bis-(1-hydroxycyclohexyl)-ethylene (IV) (m.p. 153°) and 1 g. 1,2-bis-(1-hydroxycyclohexyl)-ethane (m. 128°) were dissolved in alcohol. The solution was kept overnight and the crystals deposited were collected and dried, m. 116—118 °C. Since the m.p. is depressed, no solid solution was formed.

b, 1 g. trans-1,2-bis-(1-hydroxycyclohexyl)-ethylene (VI) (m. 103 °C) and 1 g. 1,2-bis-(1-hydroxycyclohexyl)-ethane (m. 128° C) were dissolved as above. The deposited product melted at 102 °C; the absence of m. p. depression indicates solid solution formation.

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ПРОИЗВОДСТВО СТЕРЕО-ИЗОМЕР-1,4-ЗАМЕЩЕННЫХ-БУТ-2-ЕН-1,4-ДИОЛОВ И ДОКАЗАТЕЛСЬТВО ИХ КОНФИГУРАЦИЙ

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Были сделаны эксперименты для гидрогенизации 1,4-замещенных-бут-2-ин-1,4-диолов и установлено, что при каталитически активированной гидрогенизации скорость гидрогенизации и способность к гидрорированию соединений и стереопецифичность процесса связаны с пространственным эффектом заместителей в положении 1,4.

Сравнительные данные получены на угле Pd 10%. Соединение I. при быстром гидрорировании даёт смесь. Соединение II. гидрорировая более медленно, даёт цис-олефин-диол, соединение же III. очень медленно, а при менее активном катализаторе совсем не гидрируется.

При востановлении $LiAlH_4$ было замечено, что 1,1,4,4-тетраметил-бут-2-ин гидрируется в 1,1,4,4-тетраметил-бутан-1,4-диол. А 1,2-бис-(I-гидрокси-циклогексил)-ацетилен стереоспецифично гидрируется в цис-1,2-бис (I-гидроксициклогексил)-этилен.

Пространственное строение полученных при экспериментах изомеров доказалось при помощи инфракрасной спектроскопии и применением правила Бруни.